Electronic Supporting Information (ESI)

A Sixfold Interpenetrated Microporous MOF Constructed from Heterometallic Tetranuclear Cluster Exhibiting Selective Gas Adsorption

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Experimental Section

Materials and methods.

All chemicals were commercially purchased and used as received.

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at http://www.iucr.org. The thermogravimetric analysis (TGA) was done on a standard TG-DTA analyzer under air atmosphere at a heating rate of 10 °C/min for measurement. IR spectra were measured in the range of 400-4000 cm^{-1} on a Tensor 27 OPUS FT-IR spectrometer using KBr pellets (Bruker, German). Fluorescence spectra were recorded at room temperature on a Varian Cary Eclipse fluorescence spectrometer (Varian, USA). Adsorption/desorption experiments were carried out at the temperature of liquid nitrogen (77.3 K) bath. Before the measurement, the sample of **1** was soaked in pure methanol (CH_3OH) for 3 days to remove DMF and H_2O solvent molecules, then filtrated, and activation of the methanol-exchanged **1** at 120 °C under vacuum overnight led to the formation of an activated sample **1a**. Hydrogen and nitrogen adsorption/desorption isotherms were measured using a Micromeritics ASAP 2020M volumetric gas sorption instrument and 99.999% pure N_2 and H_2.

X-ray Crystallography.

The crystallographic data of **1** were collected on a Rigaku RAXIS-RAPID diffractometer at 123(2) K with Mo-Kα radiation (λ = 0.71073 Å). The program SAINT[S1] was used for integration of the diffraction profiles. The crystal data of **1** were solved by direct methods and refined by a full-matrix least-square method on F^2 using the *SHELXL-97* crystallographic software package.[S2] In this structure, systematic absences were consistent with several space groups ($P6_3$, $P6_3/m$, $P6_322$). And the structure could also be solved and refined in $P6_3$ or $P6_3/m$ space group. However, the addsym in PLATON program[S3] or the checkcif program[S4] suggested that additional symmetry elements were found when refined in $P6_3$ or $P6_3/m$. The PLATON program implements an automatic space group search algorithm and provides the highest symmetry space group $P6_322$. Therefore $P6_322$ was selected. Anisotropic thermal parameters were used to refine all the non-H atoms. The H atoms on their parent C and N atoms in BDA and BTA ligands were fixed in geometrically calculated positions. And the H atoms on N atom of dimethylammonium ion and solvents O1w molecules cannot be added in the calculated positions. They were directly included in the final molecular formula. During the refinement of the compound **1**, the command “omit” was used to omit 3 disagreeable reflections suggesting by *. LST file. To obtain reasonable atom sites and stabilize the anisotropic displacement parameters, the “delu” and “simu” restraint instructions were used for O3, O4, C8, and O2, Cd1 atoms, respectively. Part of disordered solvent molecules including the determined DMF (N4, O5, C21-C23) and dimethylammonium ion (N5, C25, C26) were restrained using distance restraints (dfix) and thermal restraints (isor, and simu) to make the displacement parameters more reasonable. Due to the limited crystal quality, the weak high-angle diffractions, and the heavily disordered solvent molecules in the cavities, the Uiso values of disordered solvent DMF molecule (N4, O5, C21-C23) and dimethylammonium ion (N5, C25, C26) were relatively large. Combining with elemental analyses and TG analyses, we think these data are scientifically correct and can be used for the structural discussion.[S3] It should be noted that the other guest molecules (counter ions or dma) in the channels of **1** are highly disordered and could not be modeled properly, so the diffused electron densities resulting from them were removed by the SQUEEZE routine in PLATON[S4] and the results were appended to the bottom of the CIF file. The number of located electrons, 152 in four voids per unit cell, is included in the formula, formula weight, calculated density, and *F*(000). These residual electron densities were assigned to five dimethylammonium ions. So SQUEEZE removed five dimethylammonium ions per unit cell. This value calculated based upon charge balance considerations, volume/count_electrons analysis, combining with elemental analyses, and TG analyses. (One dimethylammonium ion would give 26 e). There are two formula units in one cell, so one formula unit contains 2.5 disordered dimethylammonium ions, which combining with the 1.5 determined dimethylammonium ions, giving to 4 dimethylammonium ions per formula unit. Considering charge balance, these 4 dimethylammonium ions were assigned to three dimethylammonium cations and one dimethylammonium anion. So the tentative formula for this compound is $[NH_2(CH_3)_2]_3[N(CH_3)_2][Cd_3Na(BDA)_3(BTA)_3]\cdot1.5DMF\cdot1.5H_2O$.[S3] Further details of crystal data and structure refinement for **1** were summarized in the footnote of the text. Selected bond lengths of **1** were given in Table S1. Full crystallographic data for **1** have been deposited with the CCDC (818796). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.[S5]

Reference

S1 *Bruker AXS, SAINT Software Reference Manual*, Madison, WI, 1998.

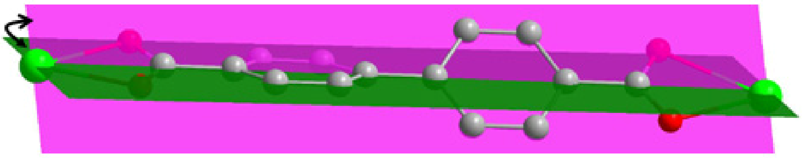
S2 (a) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

S3 (a) O. V. Dolomanov, D. B. Cordes, N. R. Champness, A. J. Blake, L. R. Hanton, G. B. Jameson, M. Schroder and C. Wilson., *Chem. Commun.*, 2004, 642; (b) Y. Du, A. L.

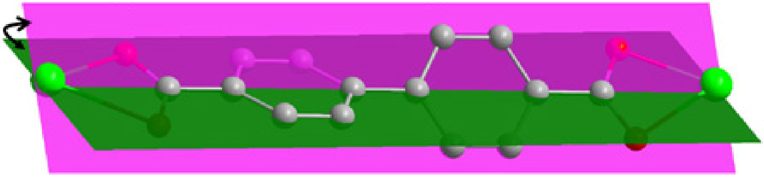
Thompson and D. O. Hare, *Chem. Commun.*, 2008, 5987; (c) Y. F. Bi, X. T. Wang, W. P. Liao, X. F. Wang, X. W. Wang, H. J. Zhang, and S. Gao, *J. Am. Chem. Soc.*, 2009, **131**, 11650; (d) W. X. Zhang, W. Xue, J. B. Lin, Y. Z. Zheng and X. M. Chen, *CrystEngComm*, 2008, **10**, 1770. and so on.

S4 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Untrecht University, 2003.

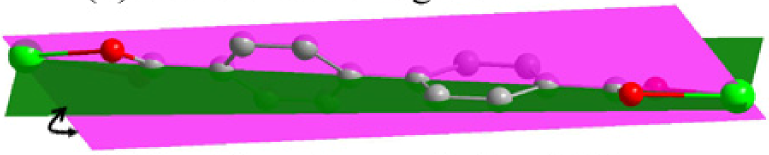
S5 The checkcif program available at: http://journals.iucr.org/services/cif/checkcif.html.



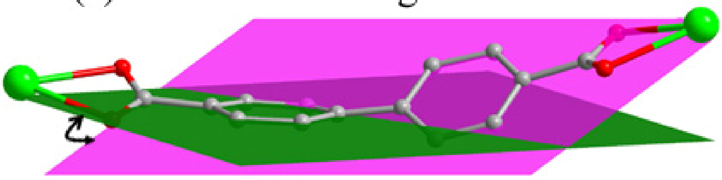
(a)The distortion angle θ_1=46.81°



(b)The distortion angle θ_2=46.79°



(c)The distortion angle θ_3=46.80°



(d)The distortion angle θ_4=38.82°

Scheme S1 Four kinds of BDA^{2-} twisted conformations and their torsion dihedral angles.

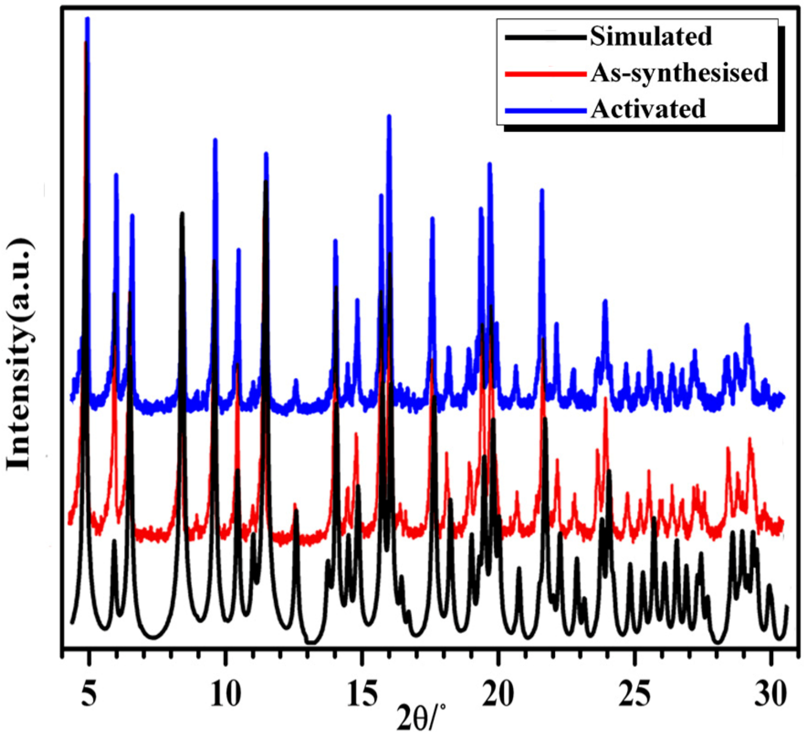


Fig. S1 XRPD patterns for **1**.

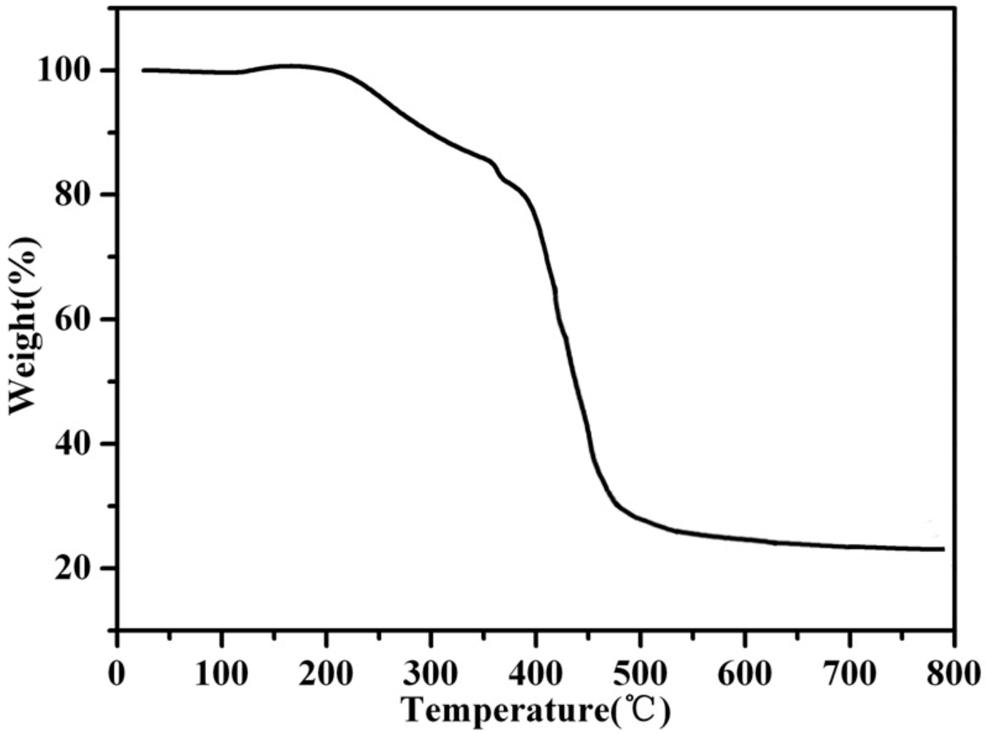


Fig. S2 TG curves of compound **1**.

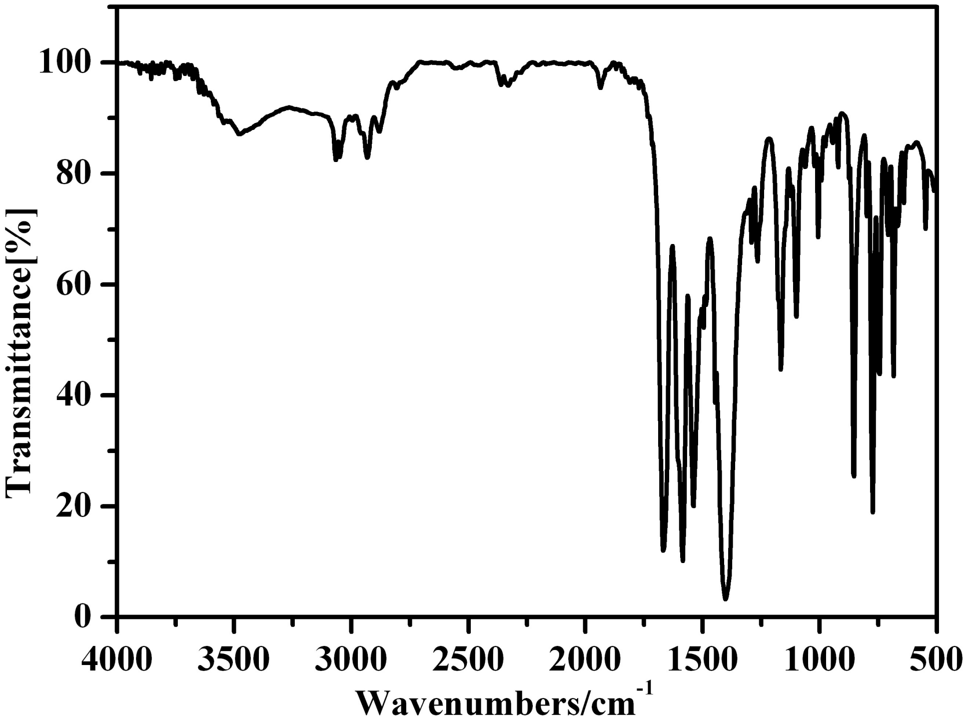


Fig. S3 IR spectra of compound **1**.

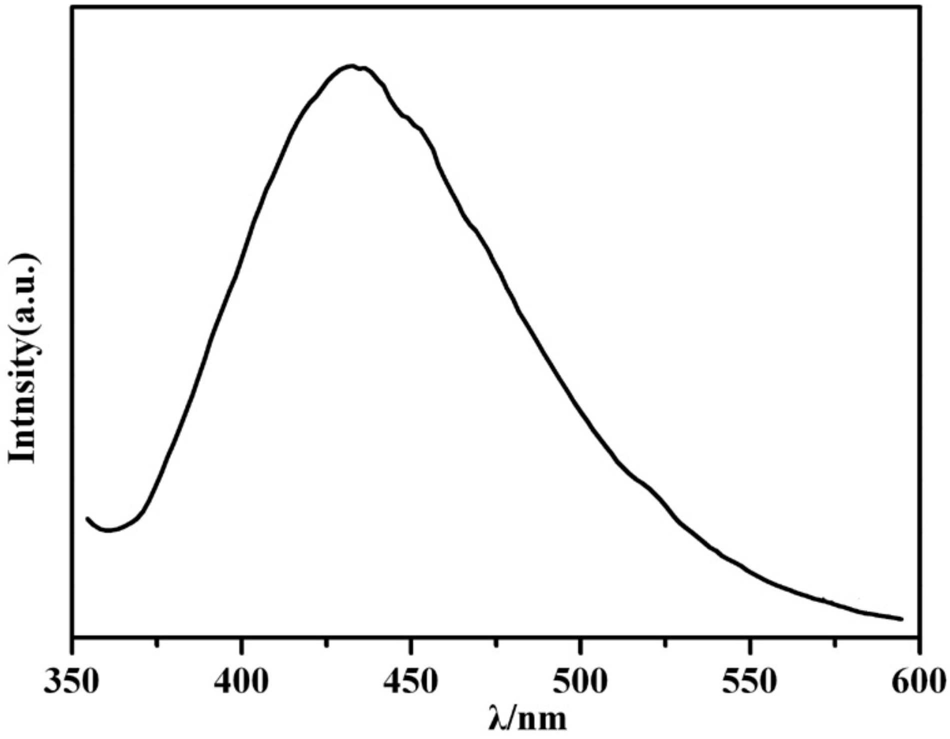


Fig. S4 Solid-state photoluminescence spectra of **1** at room temperature.

The solid-state luminescent property of compound **1** have been investigated at room temperature and the spectra are given in Fig. S4. Upon excitation at 358 nm, compound **1** exhibits strong luminescence with emission maximum at 467 nm. This observation suggests that compound **1** may be a candidate for potential blue-emitted photoactive materials. In order to understand the nature of these emission bands, we compared the emission spectra of the compound and those of free organic ligands. According to the literature reports, both free H_2BDA and HBTA ligands do not emit any luminescence in the range of 400–800 nm.[S6] The red shift of emission band occurring in **1** is probably due to ligand-to-metal charge transfer (LMCT).[S7]

Reference

S6 (a) X. Shi, G. S. Zhu, X. H. Wang, G. H. Li, Q. R. Fang, G. Wu, G. Tian, M. Xue, X. J. Zhao, R. W. Wang, S. L. Qiu, *Crystal Growth & Design*, 2005, **5**, 207; (b) K. Z. Shao, Y. H. Zhao, Y. Xing, Y. Q. Lan, X. L. Wang, Z. M. Su, R. S. Wang, *Crystal Growth & Design*, 2008, **8**, 2986; (c) Y. Y. Qin, J. Zhang, Z. J. Li, L. Zhang, X. Y. Cao, Y. G. Yao, *Chem. Commun.*, 2008, 2532; (d) X. Y. Cao, J. Zhang, Z. J. Li, J. K. Cheng, Y. G. Yao, *CrystEngComm*, 2007, **9**, 806; (e) J. Lu, K. Zhao, Q. R. Fang, J. Q. Xu, J. H. Yu, X. Zhang, H. Y. Bie. T. G. Wang, *Crystal Growth & Design*, 2005, **5**, 1091.

S7 (a) K. Balasubramanian, *Relativistic Effects in Chemistry. Part A: Theory and Techniques; Part B: Applications*, Wiley, New York, 1997; (b) C. Qin, X. L. Wang, L. Carlucci, M. L. Tong, E. B. Wang, C. W. Hu, L. Xu, *Chem. Commun.*, 2004, 1876.

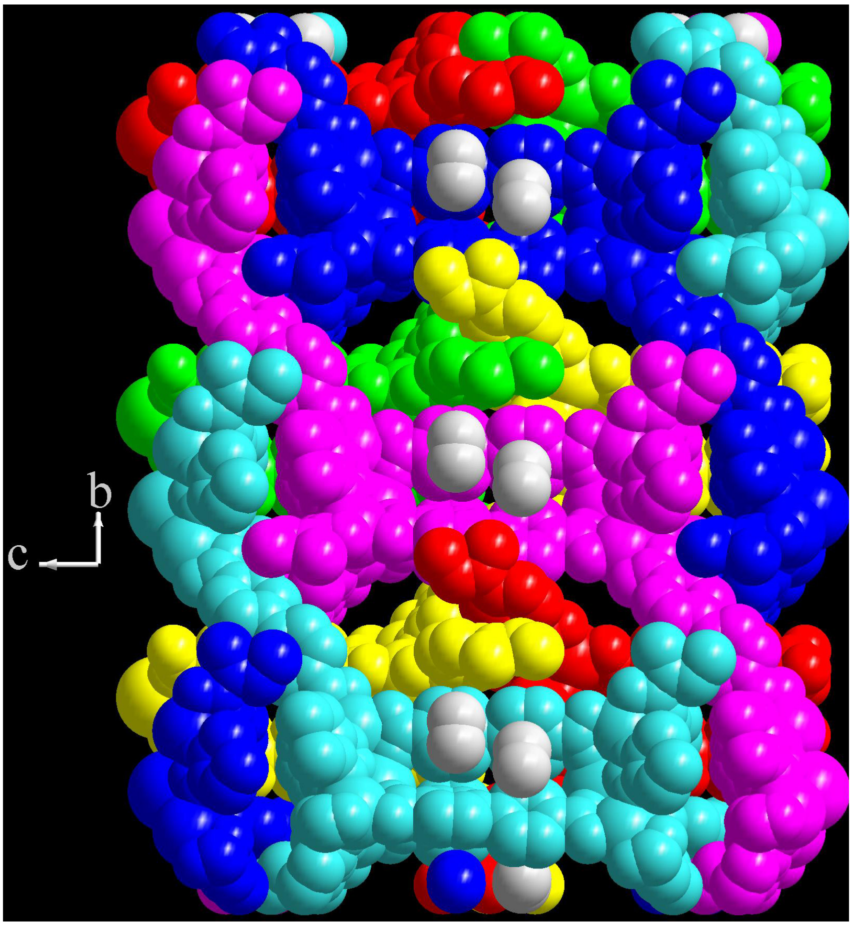


Fig. S5 A space-filling model of the sixfold interpenetration in compound **1** viewed along the *a* axis (solvent molecules omitted).

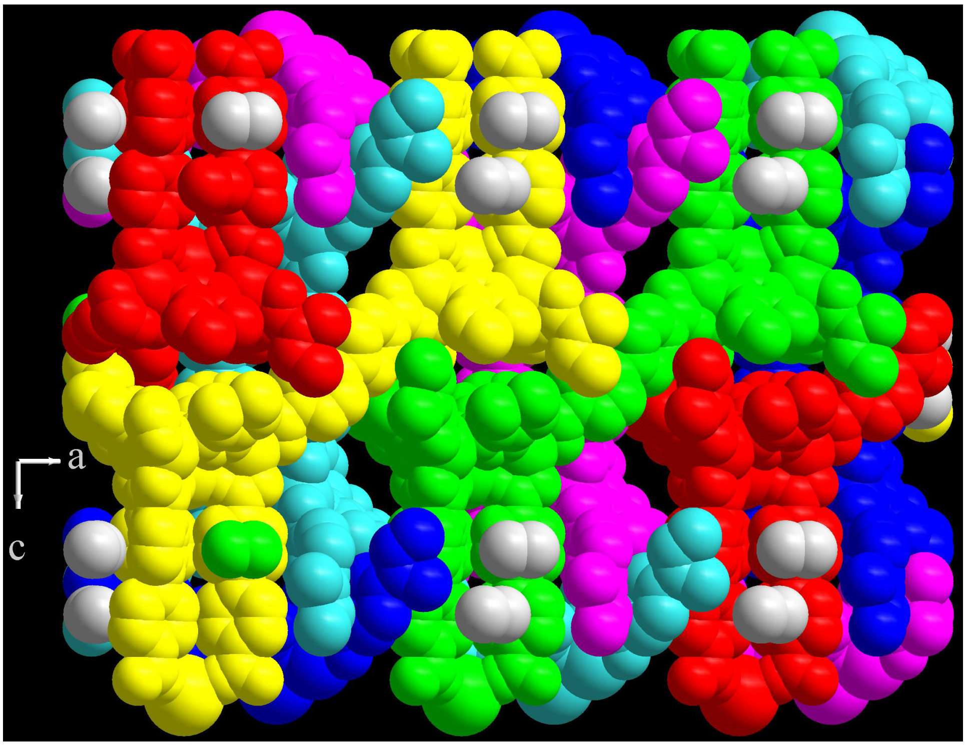


Fig. S6 A space-filling model of the sixfold interpenetration in compound **1** viewed along the *b* axis (solvent molecules omitted).

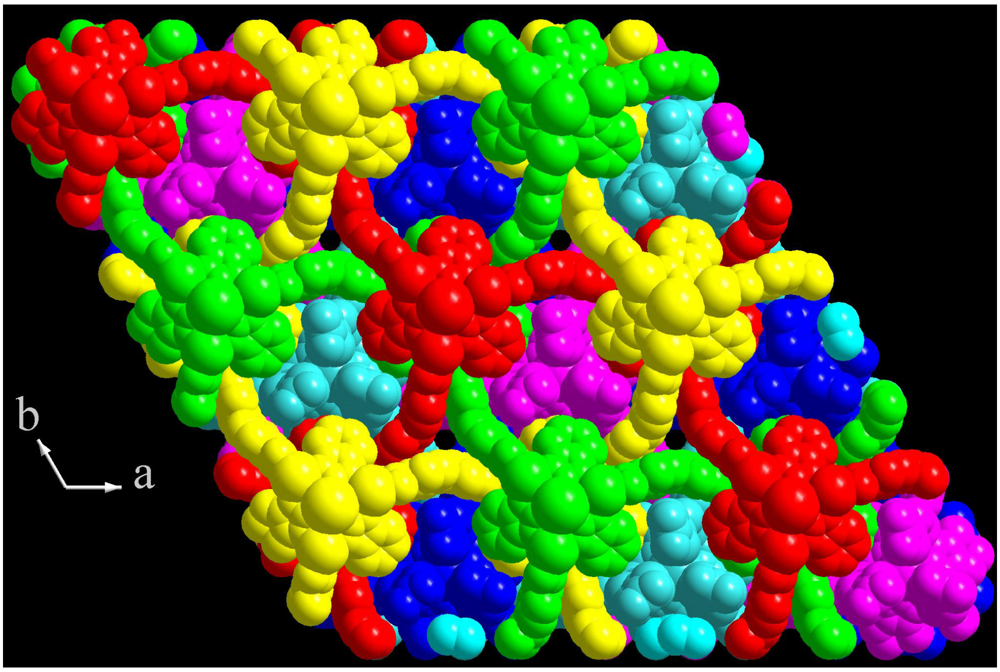


Fig. S7 A space-filling model of the sixfold interpenetration in compound **1** viewed along the *c* axis (solvent molecules omitted).

Table S1 The selected bond lengths [Å] and angles [º] of compound **1**.

Cd(1)-O(1)	2.538(5)	Na(1)-O(1)#2	2.360(5)
Cd(1)-O(2)	2.265(5)	Na(1)-O(1)	2.360(5)
Cd(1)-O(3)	2.393(6)	Na(1)-O(1)#1	2.360(5)
Cd(1)-O(4)	2.396(6)	Na(1)-N(2)#2	2.489(5)
Cd(1)-N(1)	2.252(6)	Na(1)-N(2)	2.489(5)
Cd(1)-N(3)#1	2.259(6)	Na(1)-N(2)#1	2.489(5)
N(3)-Cd(1)#2	2.259(6)		
N(1)-Cd(1)-N(3)#1	101.8(2)	O(2)-Cd(1)-O(3)	82.0(2)
N(1)-Cd(1)-O(2)	122.1(2)	N(1)-Cd(1)-O(4)	92.8(3)
N(3)#1-Cd(1)-O(2)	114.7(2)	N(3)#1-Cd(1)-O(4)	85.7(2)
N(1)-Cd(1)-O(3)	109.1(2)	O(2)-Cd(1)-O(4)	131.6(2)
N(3)#1-Cd(1)-O(3)	128.6(2)	O(3)-Cd(1)-O(4)	53.4(2)
N(1)-Cd(1)-O(1)	89.18(19)	O(1)#2-Na(1)-O(1)	105.75(14)
N(3)#1-Cd(1)-O(1)	85.31(19)	O(1)#2-Na(1)-O(1)#1	105.76(14)
O(2)-Cd(1)-O(1)	53.22(18)	O(1)-Na(1)-O(1)#1	105.76(14)
O(3)-Cd(1)-O(1)	133.9(2)	O(1)#2-Na(1)-N(2)#2	82.65(18)
O(4)-Cd(1)-O(1)	171.0(2)	O(1)-Na(1)-N(2)#2	168.1(2)
O(1)#1-Na(1)-N(2)#2	79.39(19)	O(1)#2-Na(1)-N(2)#1	168.1(2)
O(1)#2-Na(1)-N(2)	79.39(19)	O(1)-Na(1)-N(2)#1	79.39(19)
O(1)-Na(1)-N(2)	82.65(18)	O(1)#1-Na(1)-N(2)#1	82.65(18)
O(1)#1-Na(1)-N(2)	168.1(2)	N(2)#2-Na(1)-N(2)#1	90.81(19)
N(2)#2-Na(1)-N(2)	90.81(19)	N(2)-Na(1)-N(2)#1	90.81(19)

Symmetry transformations used to generate equivalent atoms: #1: -x+y+1, -x+1, z;

#2: -y+1, x-y, z